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[54] **METHOD OF DEPOSITING SHADOW
SCULPTED THIN FILMS**

[75] Inventors: **Kevin John Robbie; Michael Julian Brett**, both of Edmonton, Canada

[73] Assignees: **The Governors of the University of Alberta; Alberta Microelectronic Corporation**, both of Edmonton, Canada

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[51] Int. Cl.⁶ **B05D 5/00**

[52] U.S. Cl. **427/256; 427/248.1; 427/255.5**

[58] Field of Search **427/248.1, 255.5, 427/256**

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Primary Examiner—Roy V. King

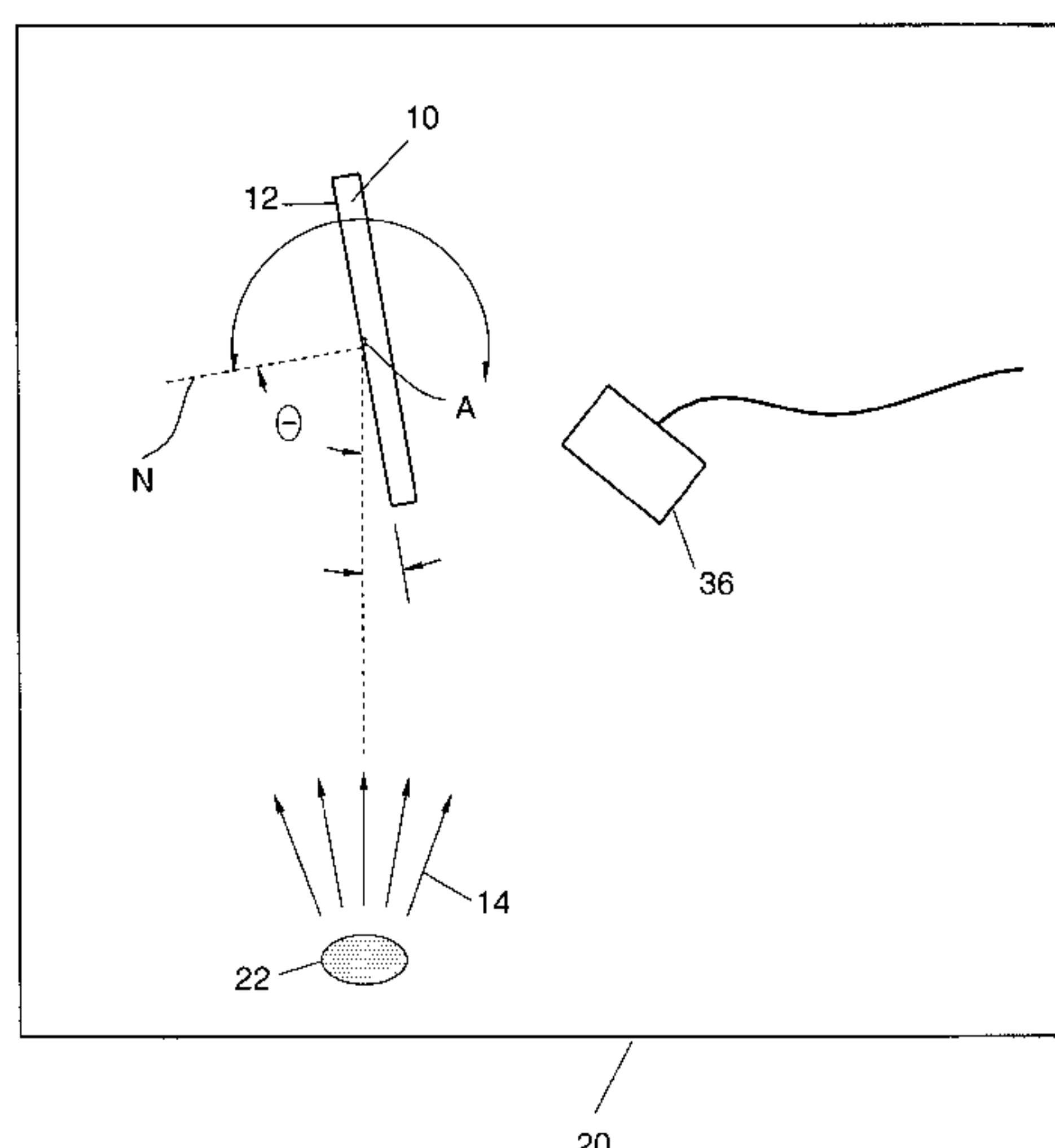
Attorney, Agent, or Firm—Anthony R. Lambert

[57]

ABSTRACT

A method of making vapor deposited thin films by rotating a substrate in the presence of an obliquely incident vapor flux. The substrate may be rotated about an axis normal to the surface of the substrate and/or parallel to the surface of the substrate by two motors mounted with their axes orthogonal to each other. Angle of incidence, measured from the normal to the surface of the substrate, exceeds 80°. Feedback from a deposition rate monitor allows control of rotation speed of both motors to produce a growth with a defined pattern.

17 Claims, 10 Drawing Sheets



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FIG. 1

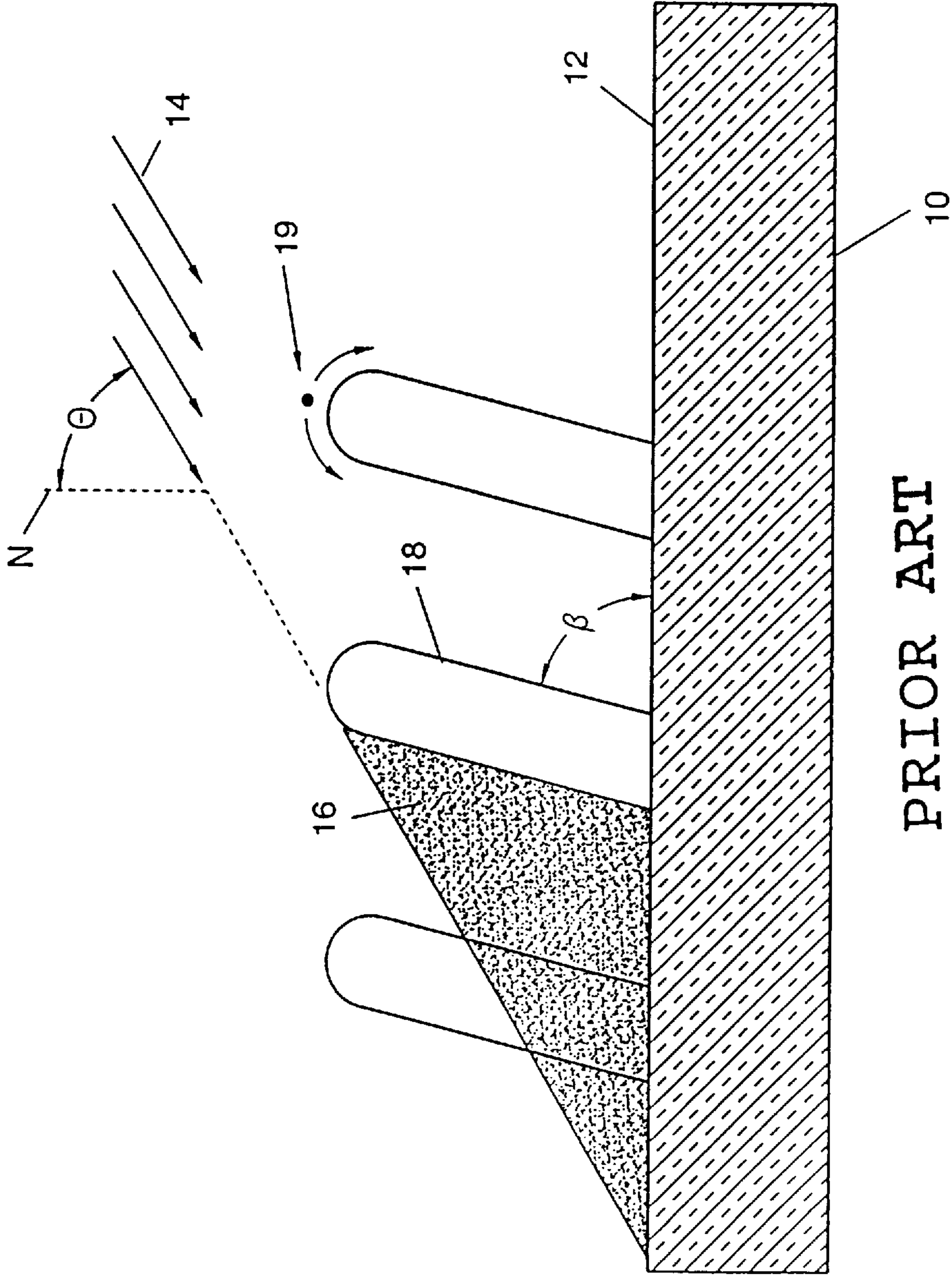


FIG. 2

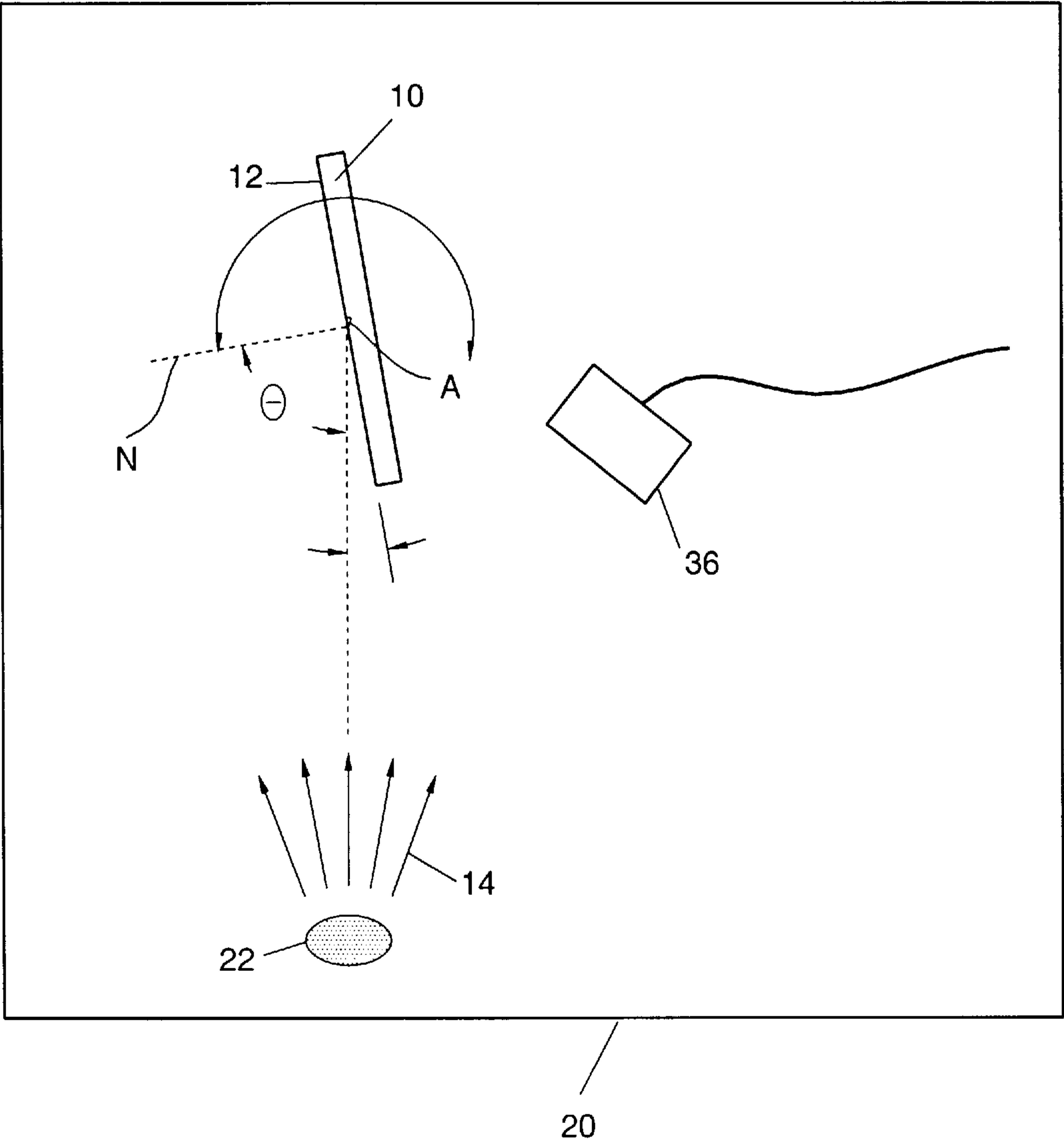
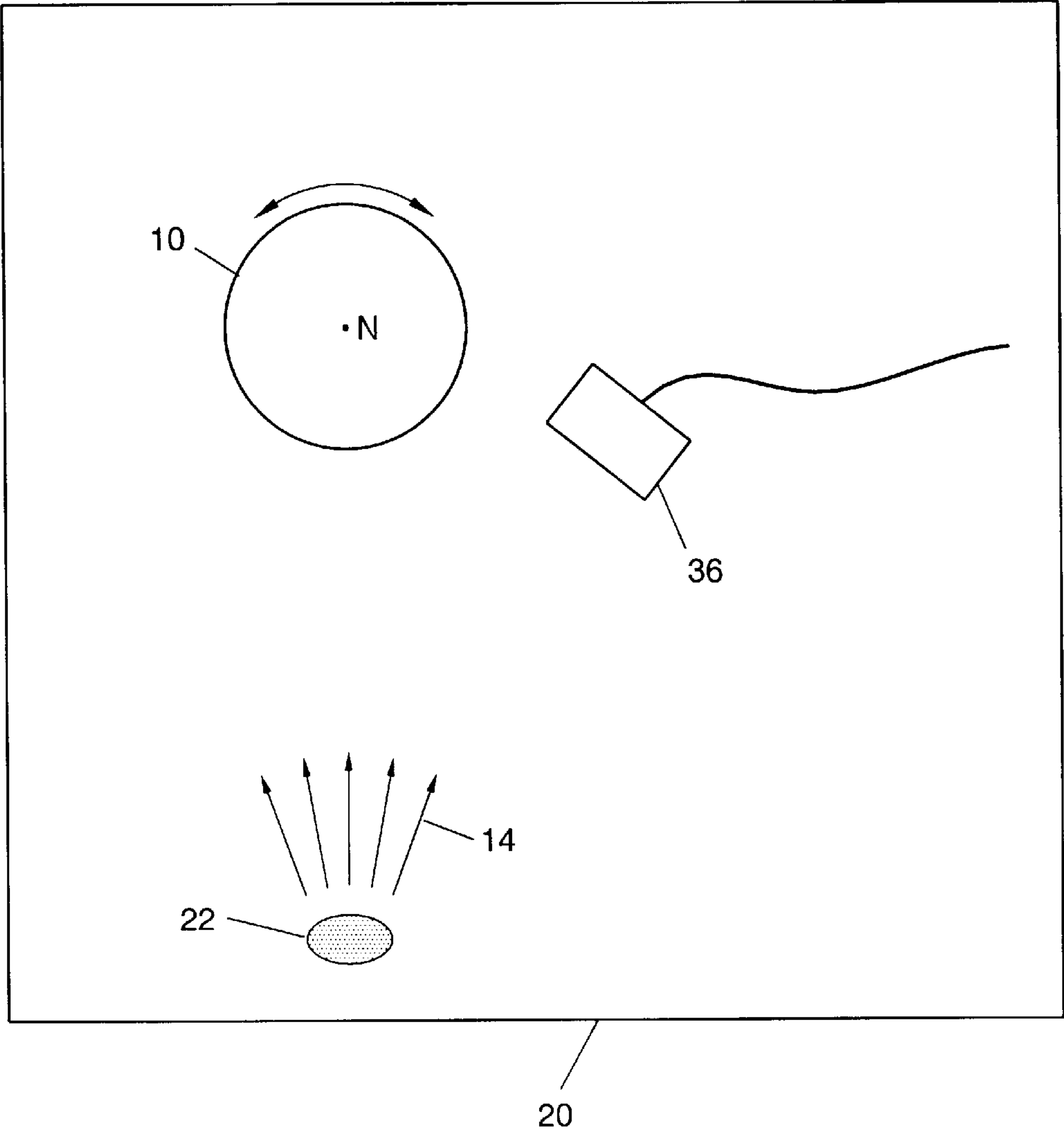


FIG. 3



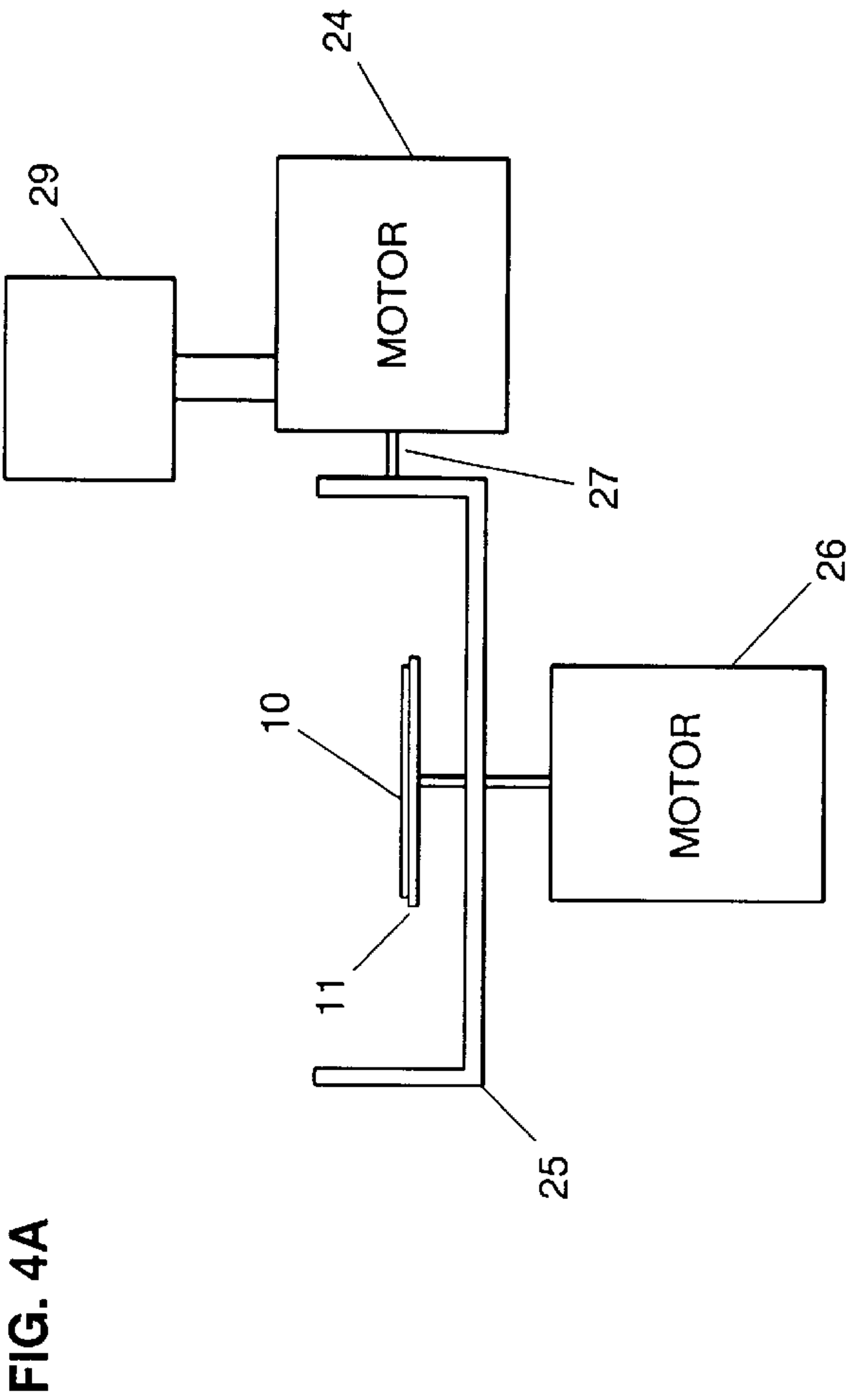
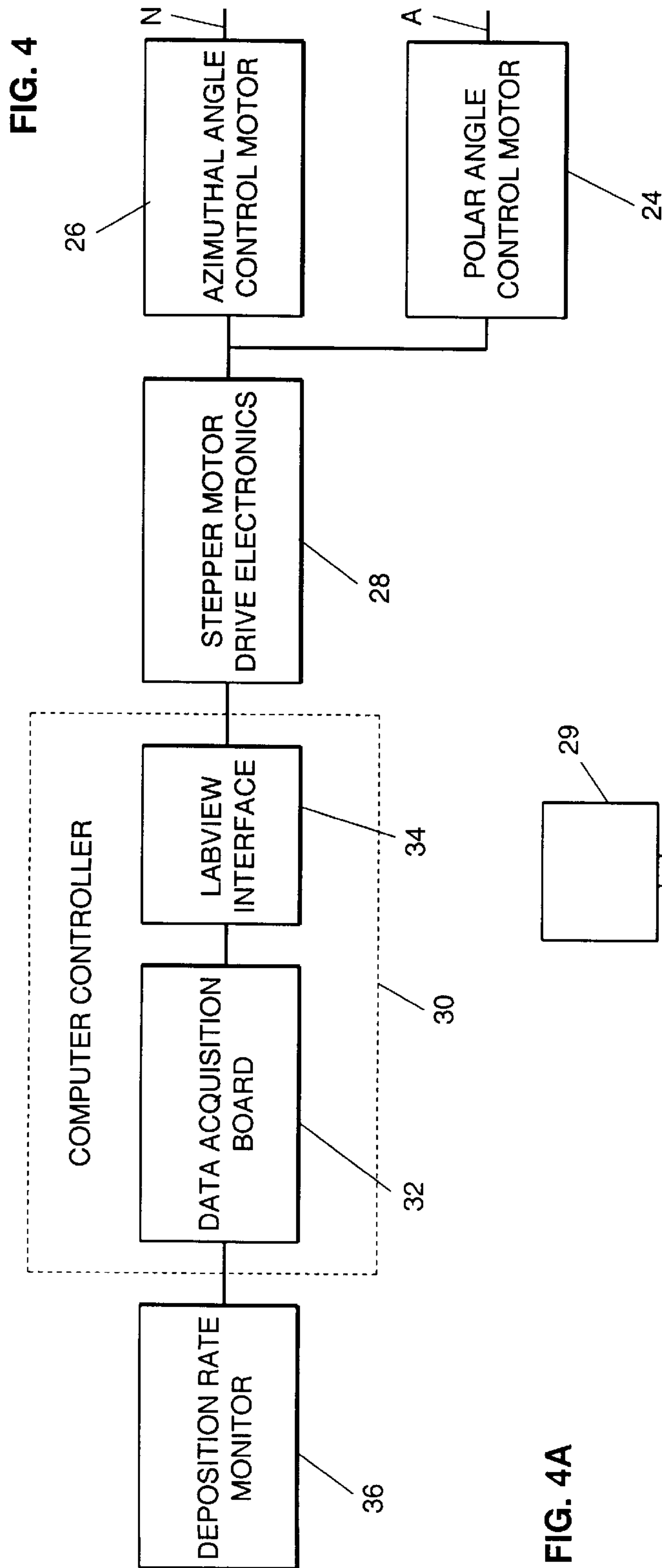


FIG. 5A

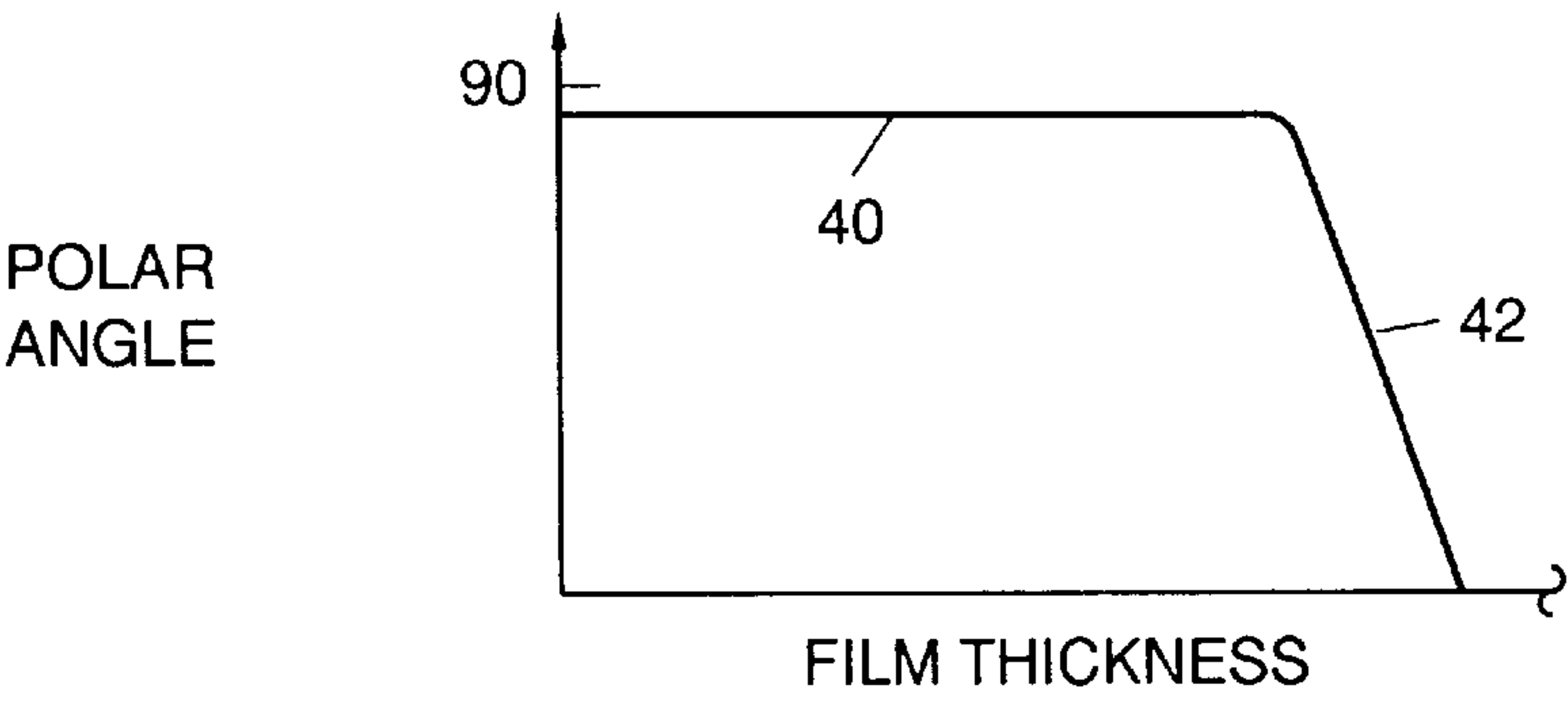


FIG. 5B

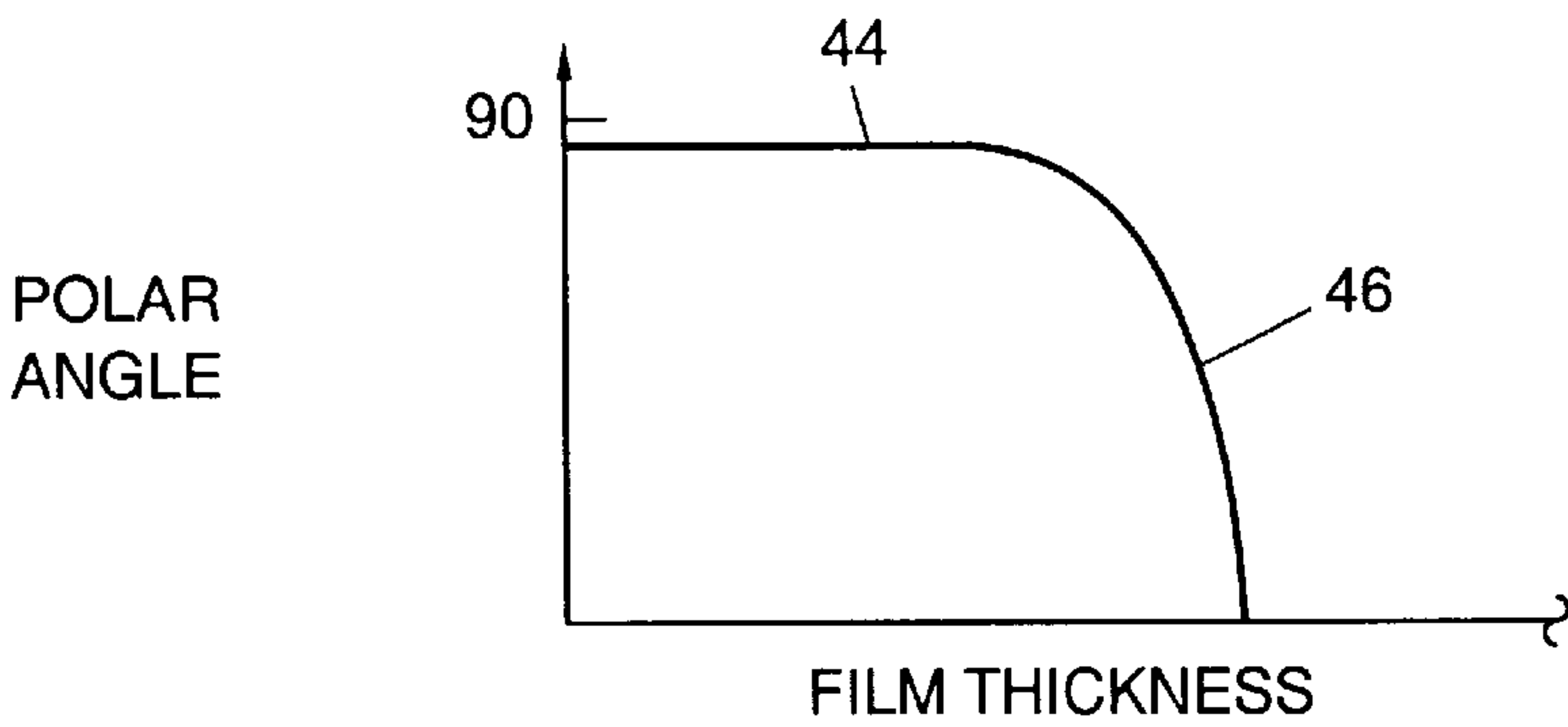


FIG. 5C

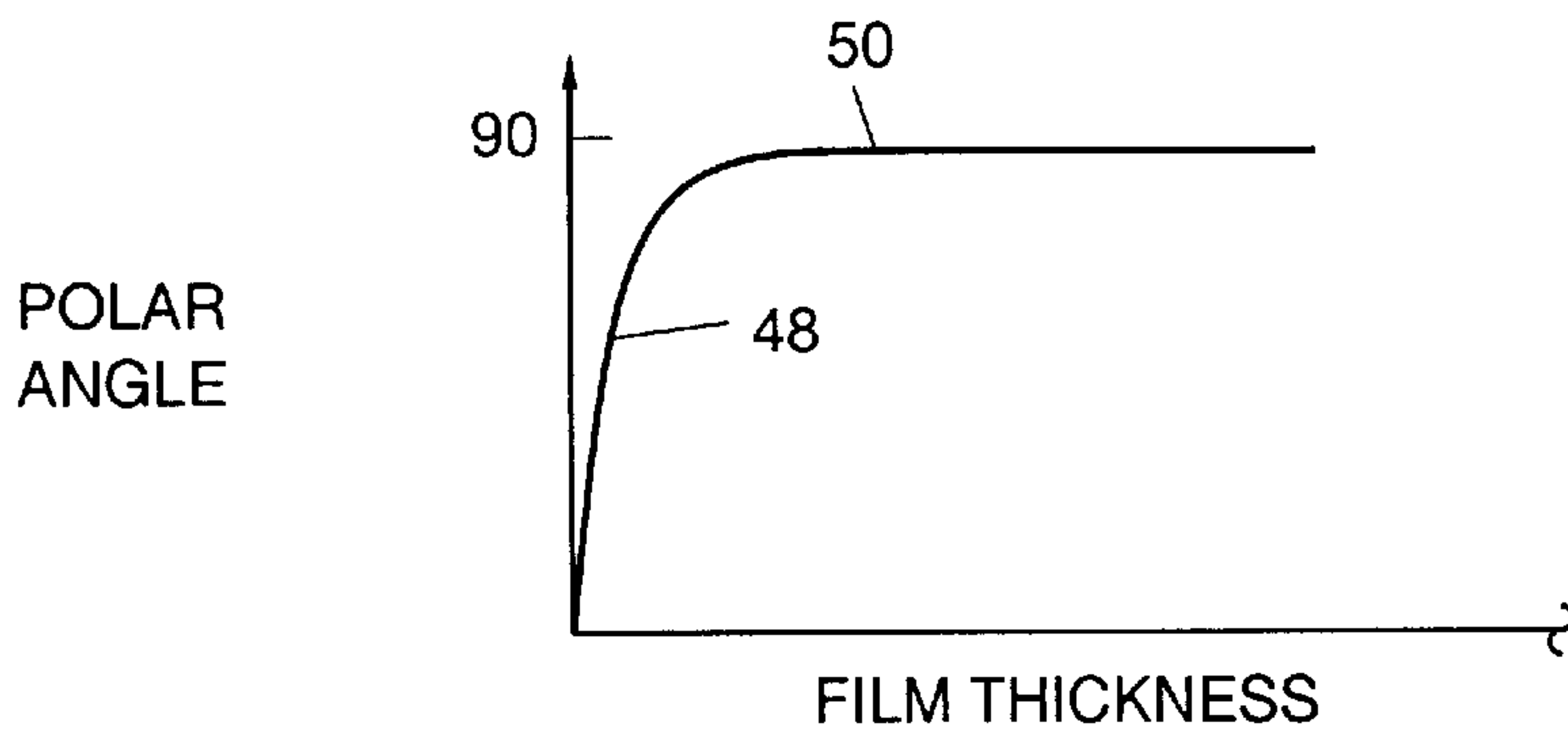


FIG. 5D

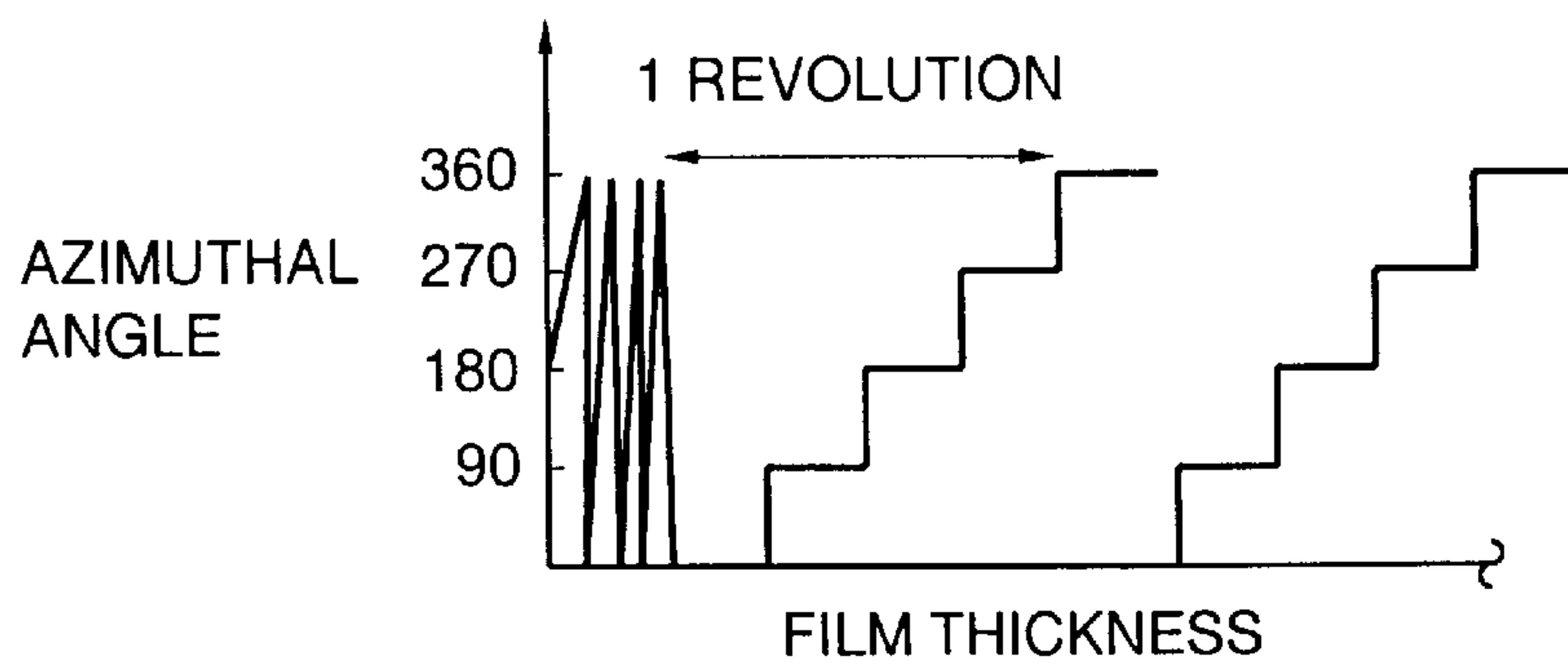
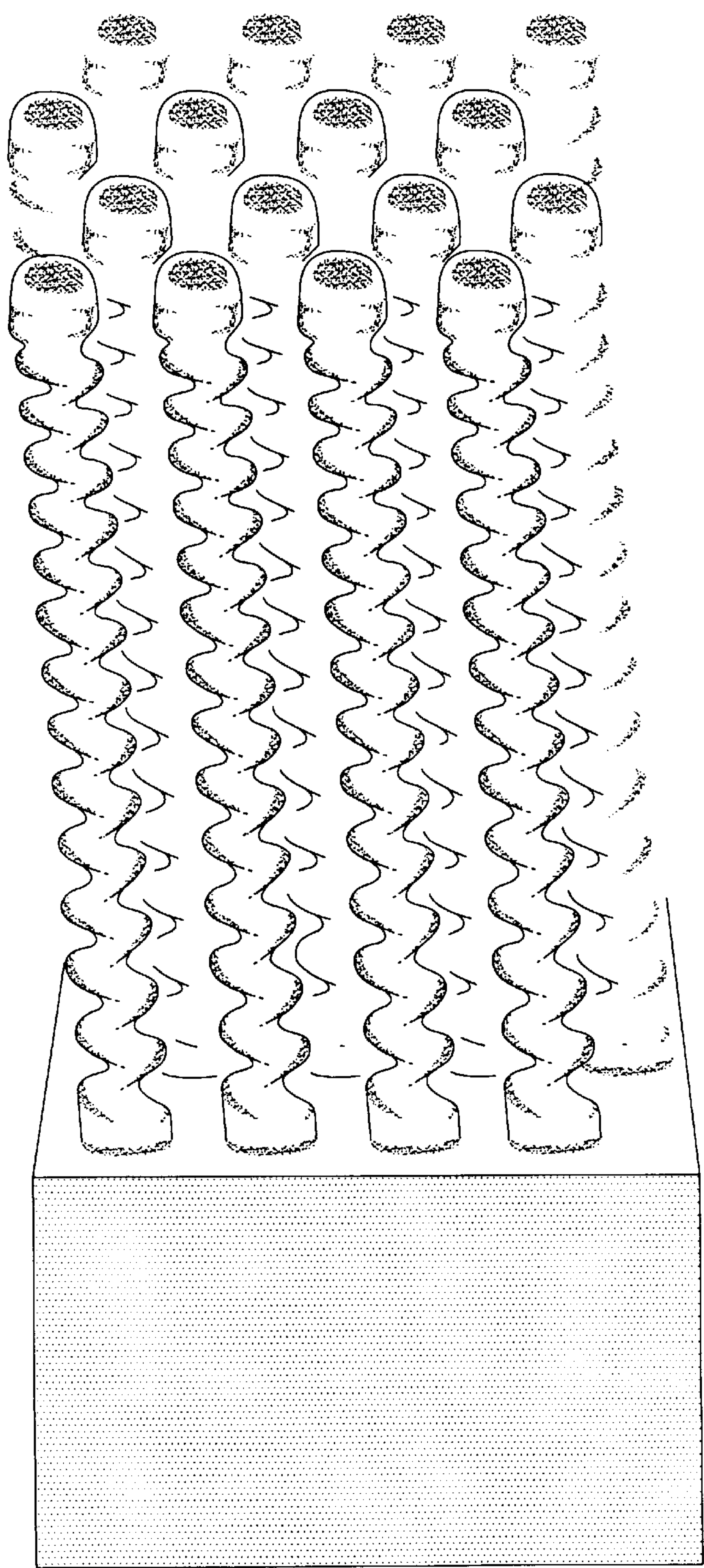


FIG. 6



5KV 1u 8 mm

FIG. 7A

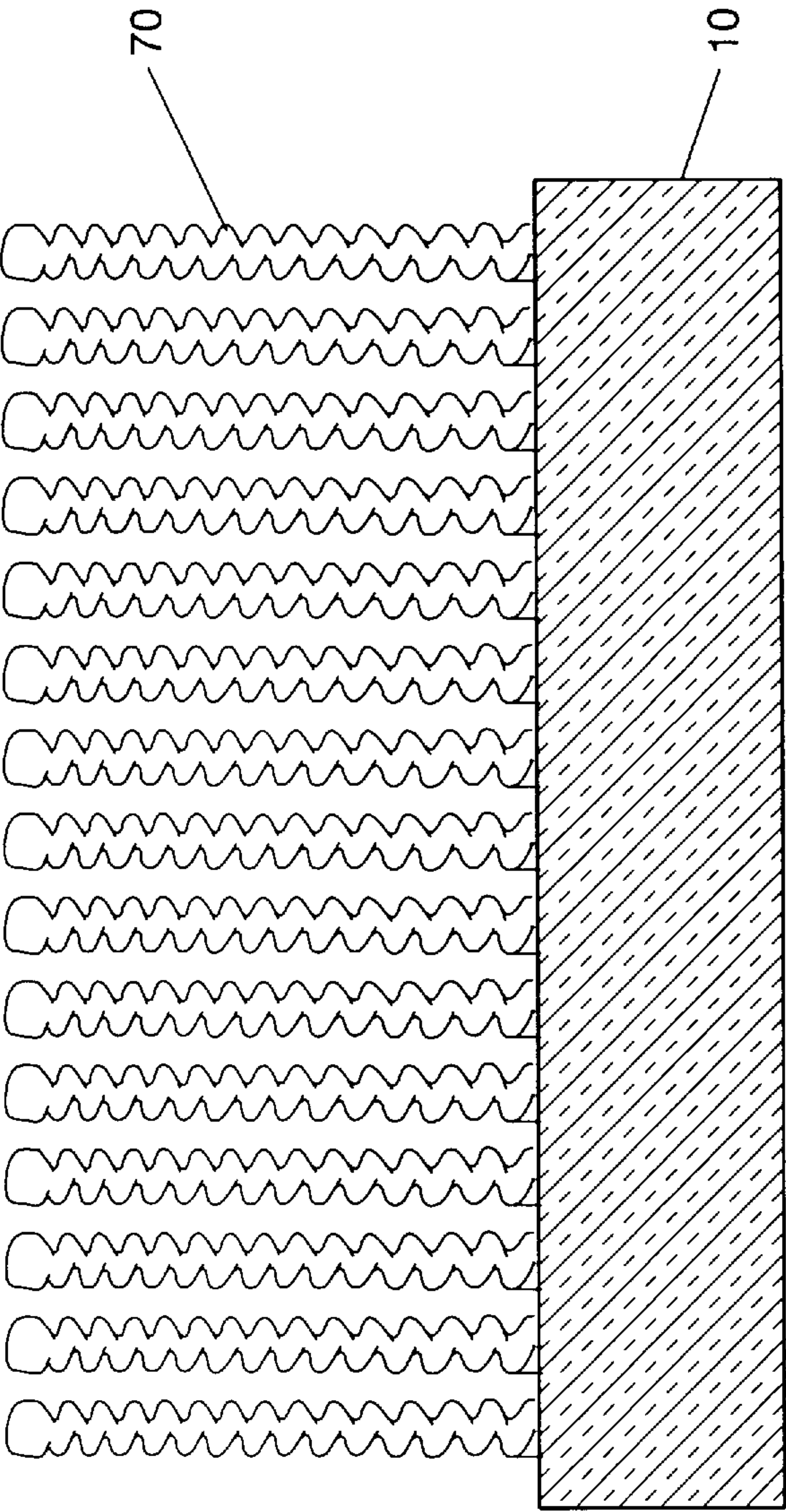


FIG. 7B

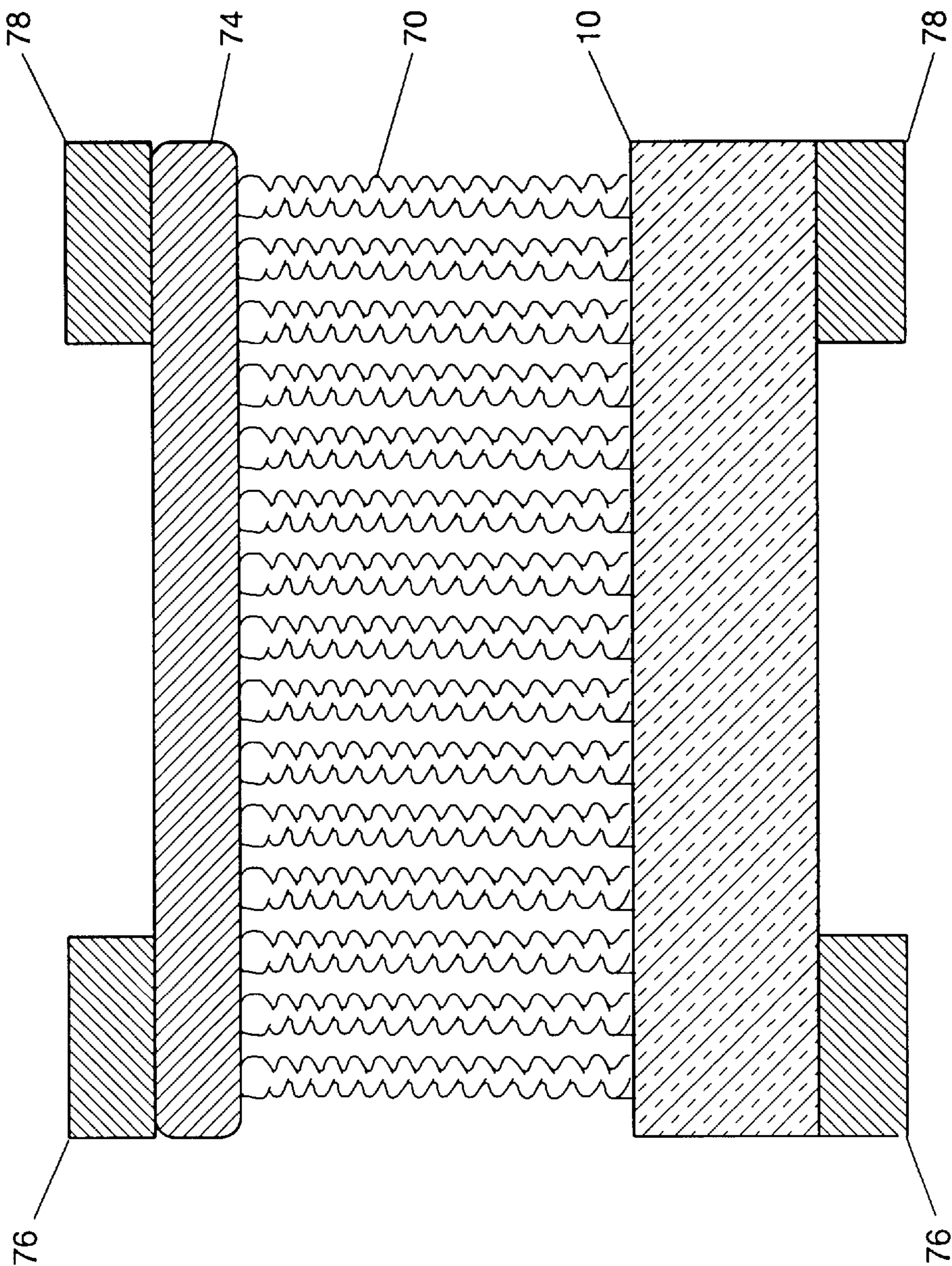


FIG. 7C

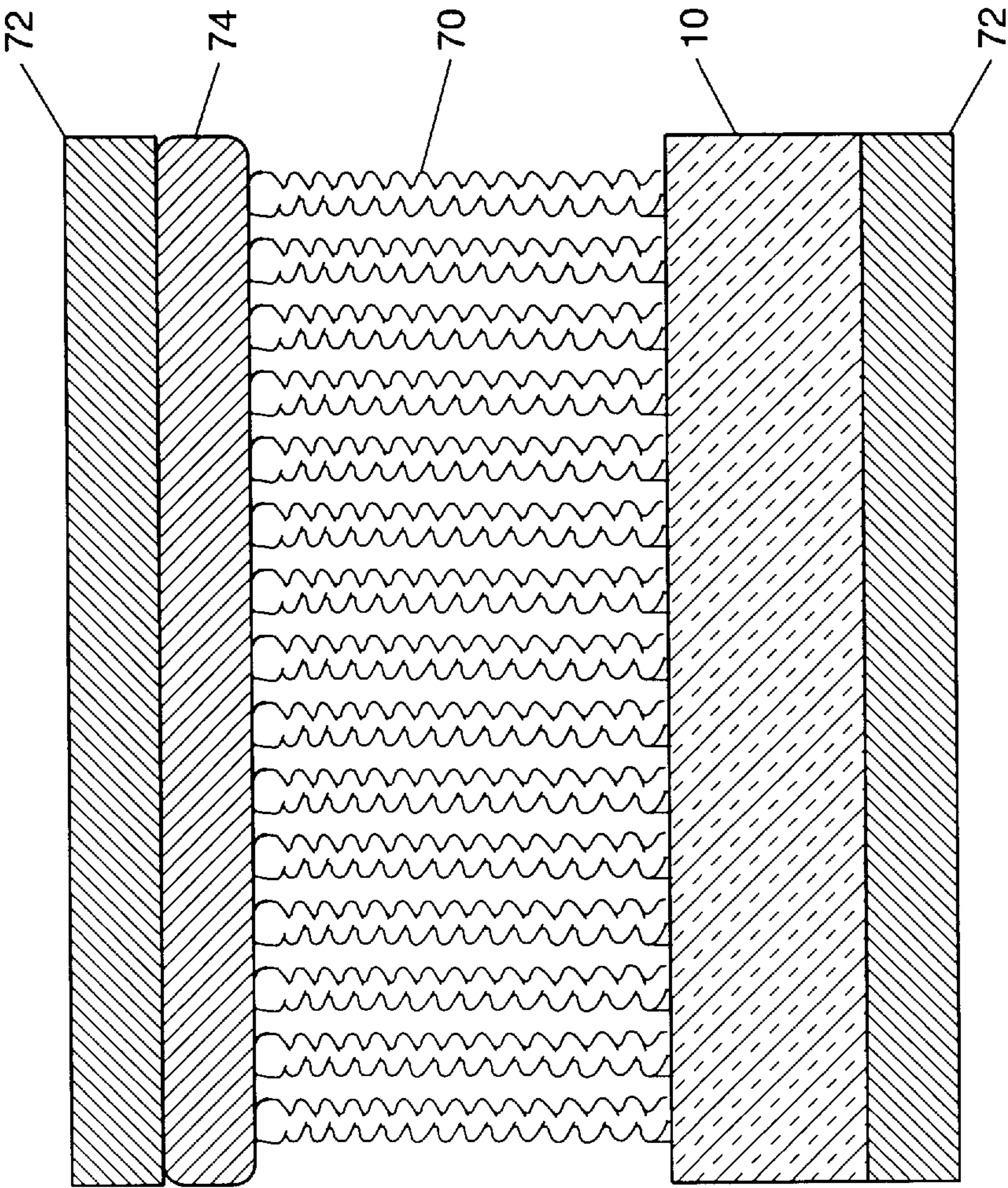


FIG. 8

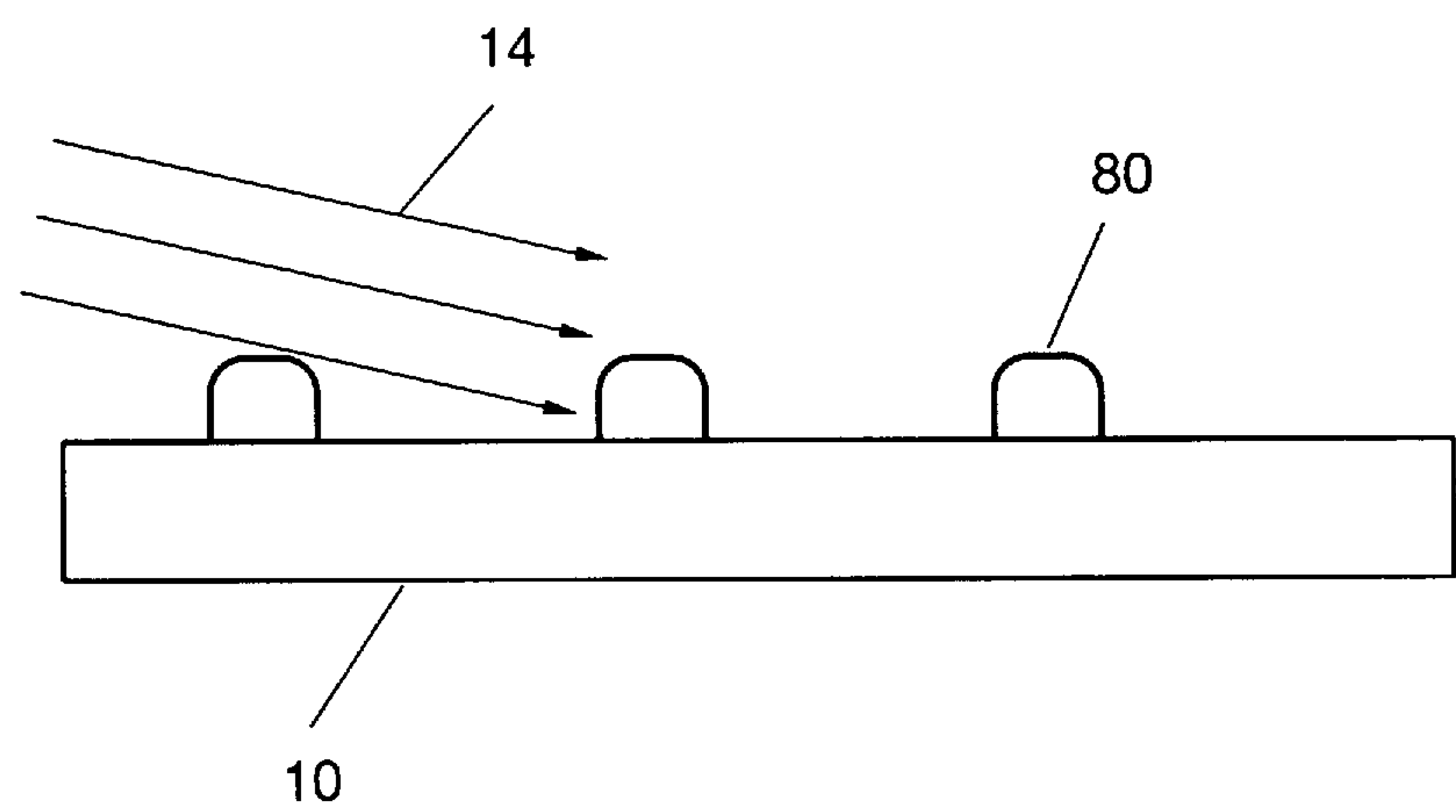
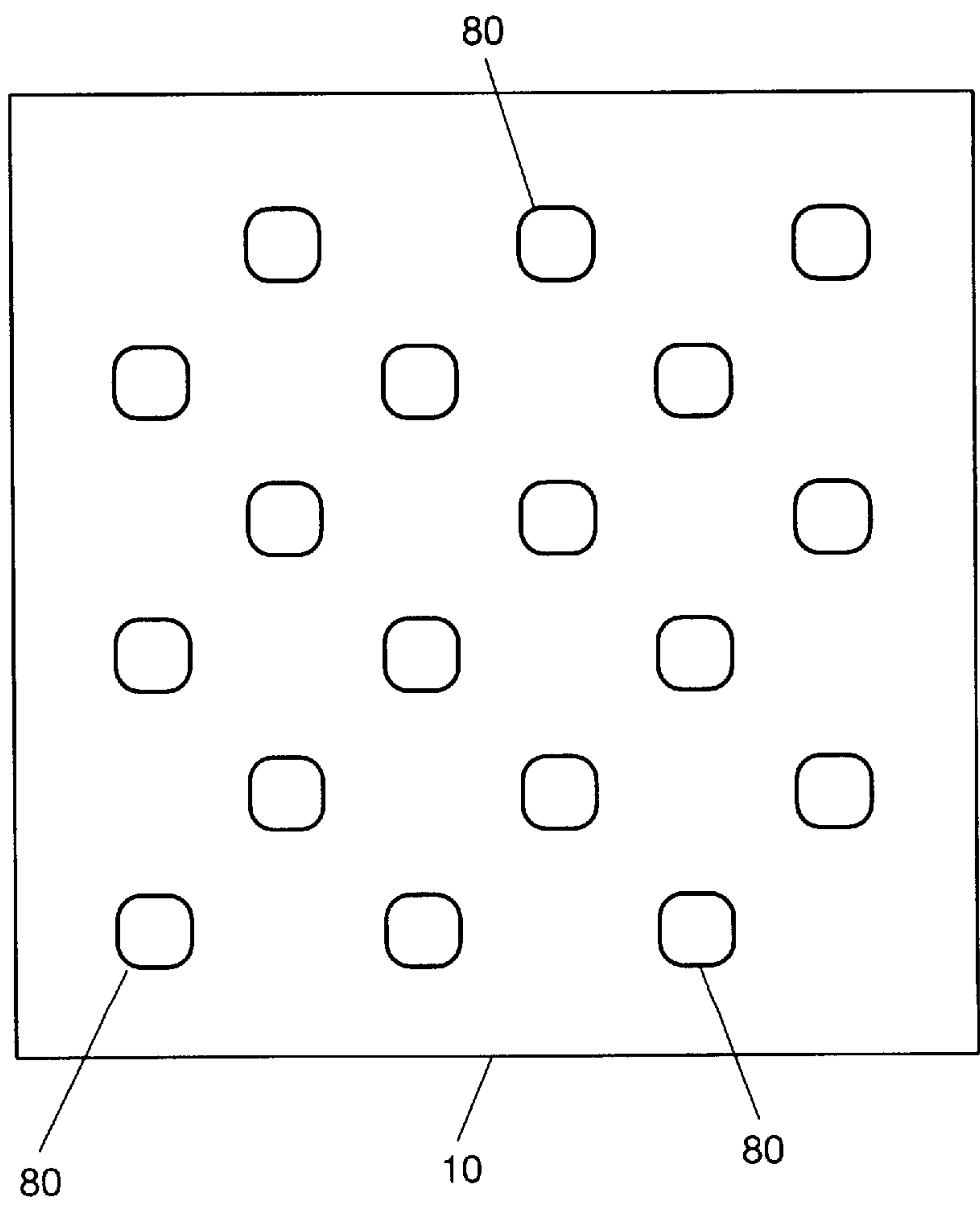


FIG. 9



METHOD OF DEPOSITING SHADOW SCULPTED THIN FILMS

FIELD OF THE INVENTION

This invention relates to the deposition of shadow sculpted thin films on substrates.

CLAIM TO COPYRIGHT

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REFERENCE TO MICROFICHE APPENDIX

A microfiche appendix containing software for implementing aspects of the method of the invention disclosed herein forms part of this patent document. The microfiche is on one sheet, and has 27 frames.

BACKGROUND OF THE INVENTION

In the art of growing thin films, it is known to expose a substrate to an oblique incident vapor flux in conditions of limited adatom diffusion and thus grow a columnar microstructure on the substrate.

The optical properties of the resulting microstructure are dependent in part on the material used, the porosity of the microstructure and the orientation of the columns of the thin film.

Hamaguchi et al, U.S. Pat. No. 4,874,664, describe lateral shifting or rotation of the position of the substrate in relation to the vapor flux to create uniform film growth and film layers that have columns with different orientations in the different layers. In Hamaguchi et al, the entire substrate is rotated in between periods of exposure of the substrate to vapor flux, or the substrate is laterally shifted during exposure to vapor flux.

The angle of the incident vapor flux in the prior art tends to be in the range from near 0° to 70° where the angle is measured between the vapor arrival line and the substrate normal, which may be referred to as the polar angle. Where the polar angle is zero, the deposited film is a uniform layer, and does not generate the columnar microstructure. For stationary substrates, results have been published for polar angles reaching close to 90°. The angle of growth of the columns is related in a way poorly understood to the angle of incidence of the vapor flux, but is always observed to be smaller, as measured from the substrate normal, than the angle of incidence.

A paper of Azzam, "Chiral thin solid films", Appl. Phys. Lett. 61 (26) 28 Dec. 1992, has proposed rotation of the substrate while it is exposed to the oblique incident vapor flux to generate a helical microstructure having helicoidal bianisotropic properties. The proposed rotation of the substrate is about an axis perpendicular to the surface of the substrate, which is referred to in this patent document as rotation about the azimuth, or variation of the azimuthal angle. No particular polar angle is specified, though a figure shows an angle of less than 60°. The inventors have attempted to grow microfilm structures by rotation of the substrate in the presence of a vapor flux incident at a polar angle of about 60° and 70°. However, the resulting structure does not show well defined structures.

The paper of Assam is a theoretical paper and fails to provide directions on how to carry out the method in

practice. In addition, the patent of Hamaguchi et al provides only one particular microstructure, with limited variation of the columnar growth.

SUMMARY OF THE INVENTION

This invention seeks to overcome some of the limitations of the prior art and provide a film forming system method and apparatus that allows for the growth of complex microstructures with predetermined patterns of growth. In addition, porosity and optical properties of the shadow sculpted thin film are enhanced by expanding the range of incidence angles of the vapor flux. Further, a method is provided for capping a porous columnar microstructure with a dense film.

Further, the inventors have found to their surprise that rotation of the substrate while it is exposed to an oblique incident vapor flux at polar angles greater than about 80° produces well defined microstructures.

Therefore, in accordance with one aspect of the invention, there is provided a method of sculpting vapor deposited thin films, the method comprising the steps of:

initially exposing a surface of a substrate to a vapor flux at an oblique incident angle to grow a columnar thin film; and

subsequently, and while continuing to expose the surface to vapor flux, rotating the substrate about an axis parallel to the plane of the substrate.

In a further aspect of the invention, there includes the step of, while initially exposing the substrate to vapor flux, moving the substrate to alter the direction of growth of the columns, as for example by rotating the substrate about a normal to the surface of the substrate to create a helical film growth. The substrate may then be rotated about an axis parallel to the plane of the substrate to form a cap for the helical thin film growth. In a further aspect, a cap may be formed by exposing the substrate to a vapor flux in conditions of high diffusion length, such that a dense uniform mass is obtained, such as by heating the substrate to nearly the melting point of the material forming the vapor flux.

In a further aspect of the invention, tailored film growths may be obtained by (a) establishing, in a computer, a desired pattern of thin film growth; (b) while exposing a surface of a substrate to a vapor flux at an oblique incident angle, changing the orientation of the surface in relation to the angle of incidence of the vapor flux; (c) providing control signals to the computer indicative of thin film growth on the substrate; and (d) automatically controlling the rate of change of the orientation of the surface in response to the control signals to grow the thin film according to the desired pattern.

In a still further aspect of the invention, there is provided a method of sculpting vapor deposited thin films, the method comprising the steps of exposing a surface of a substrate to a vapor flux at an oblique incident angle; and, at the same time, rotating the substrate about a normal to the surface while maintaining the oblique angle at greater than 80°.

In a still further aspect of the invention, there is provided an apparatus for growing thin films on a substrate having a surface, the apparatus comprising a vacuum chamber; a vapor source; a first motor disposed in the vacuum chamber above the vapor source, and having a first rotational axis, the first motor having a shaft and means for mounting a substrate on the shaft such that the first rotational axis is normal to the surface of the substrate; a driver for the first motor; a deposition rate monitor having output signals indicative of thin film growth on a substrate exposed to vapor flux from

the vapor source; and a controller responsive to the output signals for instructing the drivers to cause the first motor to rotate according to a desired pattern. According to a second aspect of the apparatus of the invention, there is also provided a second motor disposed in the vacuum chamber above the vapor source, and having a second rotational axis at about 90° to the first rotational axis. The first motor is mounted on the shaft of the second motor such that the second rotational axis is parallel to the surface of the substrate. A driver, which may be the same driver as for the first motor, is also provided for the second motor. The controller is also responsive to the output signals to cause the second motor to rotate according to a second desired pattern.

In a further aspect of the invention, a thin film microstructure is provided wherein vapor deposited material extends in distinct helical columns from a substrate. The columns may be capped, and may be supplied with electrodes to form a delay line or a variable wavelength optical filter.

In a still further aspect of the invention, the substrate may be provided with small mounds spaced sufficiently close together that growths are confined to grow on the mounds and not between them. In this way, the spacing of the helical growths can be determined in advance of deposition.

These and other aspects of the invention are described in the detailed description of the invention and claimed in the claims that follow.

BRIEF DESCRIPTION OF THE DRAWINGS

There will now be described preferred embodiments of the invention, with reference to the drawings, by way of illustration, in which like numerals denote like elements and in which:

FIG. 1 is a schematic illustrating prior art understanding of how shadow sculpting forms columnar film microstructures;

FIG. 2 is a schematic showing apparatus according to one aspect of the invention for depositing a thin film on a substrate using a vapor flux, with an exemplary substrate shown in side view, thereby illustrating how polar angle variation alters the incidence of the vapor flux;

FIG. 3 shows the apparatus of FIG. 2 with the substrate in plan view, thereby illustrating rotation of the substrate about a normal to the plane of the substrate;

FIG. 4 shows control elements for use with the apparatus of FIGS. 2 and 3;

FIG. 4A shows an arrangement of the azimuthal and polar angle control motors;

FIGS. 5A, 5B, 5C and 5D are graphs illustrating polar (FIGS. 5A, 5B and 5C) and azimuthal (FIG. 5D) angle variations;

FIG. 6 is a scanning electron micrograph showing helical columns of MgF_2 ;

FIG. 7A is a side view of a thin film with helical growths deposited on a substrate;

FIG. 7B is a side view of a thin film as in FIG. 7A with a cap, showing electrodes schematically (the electrodes are not necessarily to scale, since in practice each electrode could cover thousands of helices);

FIG. 7C is a side view of the thin film of FIG. 7B with electrode plates bounding the structure;

FIG. 8 is a side view of a substrate with mounds for pre-determining the location of helical growths; and

FIG. 9 is a plan view of a substrate with mounds showing one particular pattern of mounds.

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

FIG. 1 illustrates the physical process underlying growth of a slanted columnar film microstructure as is known in the prior art. A substrate **10**, for example a silicon wafer, has a surface **12** with normal **N** and is exposed to an oblique incident vapor flux **14** whose angle of incidence, defined in relation to the normal **N**, is θ . As atoms in the vapor flux **14** are deposited onto the substrate **10**, film growth areas atoms shadow adjacent regions **16**, preventing deposition of vapor in these regions. Atoms in the vapor flux **14** continue to be deposited in regions that are not shadowed, thus forming columns **18**. Atoms diffuse adatomically across the tops of the columns as shown at **19**. Slanted columnar microstructures will grow if the angle θ is sufficiently large to create the shadowing effect, and there is limited adatom diffusion **19**, such that adatom diffusion does not fill in the gaps between columns. In practice, angle θ need only be slightly above 0° to form reasonably defined columns and columnar structures will form in many substances at $\theta=0^\circ$, though they may be hard to discern under conditions such that the films have high atom diffusion lengths, for example due to high temperatures or materials with low melting points. The angle β of the axis of the columns **18** to the normal **N** of the substrate is less than θ . The actual relationship between θ and β is poorly understood, but approximations of the relationship are known in the art.

“Oblique” as used in this patent document in relation to an angle means sufficiently departing from 0° that atomic shadowing has an effect on the growth of columnar microstructures. The substrate may be any solid material on which a vapor may be deposited, and will depend on the application. Silicon substrates will be commonly used. The material to be deposited may be any material for which conditions are achievable to support vapor generation and deposition of the vaporized material on the substrate. In some cases, this may require cooling or heating of the substrate. To assist in bonding one vaporized material to another, an intervening layer may be first deposited, as for example using a chromium intermediate layer to bond gold to amorphous silicon dioxide (glass). The processes described here should be carried out in conditions in which the vapor flux arrives at the substrate in approximately a straight line. For this reason, it is preferred that the process be carried out under conditions approximating a vacuum, at less than 10^{-3} torr, for example at 10^{-6} torr. At higher pressures, scattering from gas molecules tends to prevent well defined structures from growing. In addition, the material used should have a sticking co-efficient of at least about 0.9 to enable the formation of distinct structures.

Referring now to FIGS. 2, 3 and 4, an apparatus according to the invention is shown for growing a thin film on a substrate **10** having a surface **12**. A conventional vapor source **22** is located within a vacuum chamber **20**. A conventional shutter (not shown) located above the vapor source **22** is used to control whether or not the substrate **10** is exposed to vapor. Various conventional means (not shown separately) for causing the vapor source **22** to emit a vapor flux **14** may be used. A substrate **10** is supported in the vacuum chamber **20** on a motor **24** (FIG. 4) disposed in the vacuum chamber **20** above the vapor source **22**. The motor **24** rotates the substrate about an axis **A** lying parallel to and preferably in the plane defined by the surface **12** of the substrate **10**. Rotation of the substrate **10** about axis **A** alters the polar angle, namely the angle of incidence θ of the vapor flux **14**. Motor **26**, also disposed in the vacuum chamber **20**

above the vapor source **22**, has a rotational axis coinciding with the normal **N** of the substrate **10** and thus alters the azimuthal angle. The polar angle and the azimuthal angles are both measures of the orientation of the surface of the substrate to the incident flux.

As shown in FIG. 4A, the substrate **10** is preferably mounted on a disc **11** which is attached to motor **26**. Various mounting arrangements of motor **24** and motor **26** may be used. For example, motor **26** may be mounted on a frame **25**, and the frame **25** may be mounted to rotate with the drive shaft **27** of motor **24**. Motor **24** itself may be mounted by any of various conventional methods for mounting motors within a vacuum chamber such as on a support **29**.

Referring now to FIG. 4, motors **24** and **26** are preferably conventional stepper motors driven by stepper motor drive electronics **28** and controlled by computer controller **30**. The computer controller **30** includes a data acquisition board **32** and a software based interface **34** such as LabVIEW™ available from National Instruments. The data acquisition board **32** receives signals indicative of thin film growth on the substrate output from a deposition rate monitor **36** of conventional construction located within the vacuum chamber **20** in a location in which film growth on the deposition rate monitor **36** is representative of film growth on the substrate **10**. In response to receiving the output signals from the deposition rate monitor **36**, the computer controller **30** instructs the driver **28** to cause the motors **24** and **26** to rotate according to a desired pattern. As described herein, the computer automatically controls the rate of change of the orientation of the surface in response to the output control signals to grow the thin film according to the desired pattern. An exemplary software program for programming the computer controller **30** using LabVIEW™ software is contained in the microfiche appendix. Start and stop signals for vapor deposition may be sent by the computer to a drive for the shutter for starting vapor deposition, or the shutter may be opened manually. Normally, the motors are started before the shutter opens to initiate deposition.

The software receives a deposition rate from the deposition rate monitor. The actual thickness (T_2) of the film growing on the substrate is related to the thickness on the deposition rate monitor by an empirically determined scaling factor known as the tooling factor. The software also knows the motor positions at the last time instant (X_{fi} for motor **24**, X_{ci} for motor **26**) and receives as input from the operator, the number (N) of turns to be made by the motor **26**, the tooling factor (ratio of vertical film growth rate to measured deposition rate), an initial deposition rate estimate, an initial angle of incidence for the vapor flux during sculpted film growth, motor rotation direction, and various parameters that define the desired pattern of growth for the film. The inputs to the computer establish the desired pattern of film growth.

In the case of formation of helical film growths, the pitch w of the helix must be specified, and in the case of a capping layer for a film growth, both the cap thickness (T_c) and number of turns (N_c) of the motor **24** must be specified by the operator.

In an embodiment of the invention, the motors **24**, **26** are step motors that rotate a fraction of a circle each time instant, t_i , t_{i+1} , t_{i+2} etc. At any given time t_i , the computer has just updated the thickness of the film from the deposition rate monitor **36** and changed the motor step rate so that at t_{i+1} , the motor **24**, **26** will be at approximately the desired position according to the desired pattern. Between time instants t_i and t_{i+1} , the software calculates what the thick-

ness of the film growth will be at t_{i+2} and calculates how fast the motors must rotate in order to give the desired thickness at t_{i+2} . At t_{i+2} , the computer then reads the new thickness from the deposition rate monitor as well as the motor stepping rates, and adjusts the motor stepping rate so that at t_{i+3} the film growth pattern will be approximately as desired. The software continues in this fashion until a stop signal is received, for example when the film has reached a desired thickness.

Algorithms for controlling the motors **24**, **26** in the case of a helical film with a cap are incorporated in the microfiche appendix, and illustrated graphically in FIGS. 5A–5D. For the motor **26**, if helical film growth has not reached the desired thickness, that is, T_2 is less than $w*N$, where $*$ indicates multiplication throughout this patent document, then X_{c2} is $360^\circ/w*T_2$, that is, the substrate **10** is rotated to a position equal to 360° times the ratio of T_2 to w . If T_2 is greater than or equal to $w*N$, that is, the helical film thickness has been achieved, then during a capping process, X_{c2} is $360*N+360*N_c/T_c*(T_2-w*N)$, that is, X_{c2} gradually increases from $360*N$ to $360*(N+N_c)$ proportionally to the capping layer thickness (T_2-w*N). This rotation rate will typically be faster than the rotation rate during helical film growth, depending on the choice of the factor N_c/T_c .

For the motor **24**, if helical film growth has not reached the desired thickness, the motor **24** does not change position, hence polar or flux angle remains the same. If T_2 is greater than or equal to $w*N$, then the new motor position X_{f2} equals the motor position at the last time instant (X_{fi}) plus $(90-X_{fi})$ times the ratio of the difference of T_2 from $w*N$ to the thickness of the cap (that is, $X_{fi}=X_{fi}+(90-X_{fi})/T_c*(T_2-w*N)$).

This last formula is represented graphically in FIG. 5A. The polar angle (angle of incidence measured from the normal) is kept constant over an initial period **40**, during which the surface of the substrate is exposed to oblique incident vapor flux, and then rotated at a constant angular rate to zero, while continuing to expose the surface to vapor flux. Changing of the polar angle towards zero produces a cap for the sculpted film growths. At zero polar angle, the flux is normally incident. The algorithm for controlling the azimuthal angle results in the substrate rotating N times to achieve a helical film growth of thickness $T_2=w*N$. During the capping process, the substrate continues to rotate about the azimuth, typically, but not necessarily, at a faster rate than during helical film growth. During the period **40**, the substrate **10** may be (a) rotated about a normal to its surface to create helical microstructures, (b) shifted 180° to form zig-zags, (c) translated, (d) kept at a constant orientation to the vapor source, or (e) otherwise rotated or translated to obtain a desired growth pattern under the cap.

Alternatively, the cap for a film growth may be created by exponentially decreasing polar angle as illustrated in FIG. 5B. The algorithm for controlling the polar angle is the same during helical film growth as for the linear cap: the angle is kept constant. During capping, X_{f2} is assigned the value X_{fi} plus $(90-X_{fi})$ times e raised to the power of $((T_2-w*N-T_c)/k)$, where k is the exponential scale factor or time constant (for example, 800). Hence, the polar angle drops monotonically from near 90° to zero as T_2 approaches the sum of $w*N$ (the desired thickness of the columnar layer) and T_c (the thickness of the cap). As illustrated in FIG. 5B, polar angle is constant during helical film growth (area **44**) and exponentially decreasing to zero in area **46**. Rotation speed of the substrate about its normal depends in part on the deposition rate. For MgF_2 at 85° angle of incidence, and a pitch of about 50 nm, the speed is about 2 rpm. Typical

rotation speeds used in the process are about 0.2 to 3 rpm. For higher deposition rates, higher speeds will be possible, but the speed should not be so high so as to destroy the distinct columnar features produced by the invention.

FIG. 7A illustrates a thin film microstructure produced by the process described here with rotation of the substrate about a normal to the substrate. Vapor deposited material extends in distinct (separate from one another) helical columns **70** from the substrate **10**. FIG. 7B illustrates the same thin film with the distinct helical columns **70** terminating distally from the substrate **10** in a region of denser material forming a cap **74** for the helical columns. The cap **74** may be produced by changing the angle of incidence of the flux from θ near 90° to zero (as in FIG. 2) as described above (corresponding to rotation about an axis parallel to the substrate surface), or, it is believed on reasonable grounds that, the deposition of the helical columns may be ended under conditions giving rise to a higher diffusion length, as for example higher substrate temperature or changing to a lower melting point material. Increased substrate temperature may be created by exposing the substrate to light from quartz lamps. Temperatures of within about 100°C. to 200°C. of the melting point of the material being deposited may be required to create conditions of high diffusion length.

In these cases, the substrate **10** is planar. If the substrate **10** is not planar, a mask may be used to expose the substrate **10** to vapor only through slits in the mask and thus control the angle of incidence of the vapor. The mask may then be moved across the substrate to produce the desired thin film by sequential exposure of different portions of the substrate.

The desired pattern of film growth may also be tailored further. For example, a film may be started with a planar film of low porosity by rotating the substrate through exponentially increasing polar angles (zero to near 90° , as seen in FIG. 5C, area **48**), with rapid azimuthal rotation (FIG. 5D), and then columns may be grown on the substrate **10**, with or without rotation. In one embodiment of a tailored growth pattern, the substrate **10** is maintained at a constant polar angle (area **50** in FIG. 5C) while the substrate is repeatedly (a) rotated azimuthally a set number of degrees, for example 90° , and (b) held at a constant azimuthal position while the film grows obliquely, but linearly. The result is a helix with square sides in this instance. In general, the number of sides of the helix is $360/\gamma$, where γ is the number of degrees the substrate is rotated during periods of deposition.

In a further variation, the rotation of the motor **26** may be reversed during deposition to produce helices with sections of different handedness, one section having a right handed twist, and the other a left handed twist.

Since the deposition rate tends to vary considerably during deposition, to achieve helical growths with constant pitch, the rotation speed may need to be increased and/or decreased during deposition. In addition, by increasing/decreasing rotation relative to the deposition rate, helices with reduced/increased pitch, or helices with graded pitch may be obtained.

In general, the polar angle during an initial deposition period in which helical microstructures are to be produced should be greater than about 80° . The following table shows density of substances deposited as an obliquely incident vapor flux onto a substrate rotating about a normal to the surface of the substrate. The density given is the measured density of the helical film as a percent of the density of a planar film deposited at zero polar angle (normal incidence).

TABLE 1

Substance	Polar Angle in Degrees	% Density
Cu	85	46
Cu	88	37
MgF ₂	85	32
CaF ₂	75	19
CaF ₂	85	9.3
SiO	85	32
SiO	88	22
SiO	85	42
SiO	75	89
Al	85	32
Mn	85	52
Cr	85	27
Ag	85	52

While the porosity of CaF₂ at a polar angle of 75° is high, CaF₂ exhibits apparently poor structural features at 75° . The high porosity is believed to be due to the fact that CaF₂ molecules have extremely low surface mobility and thus, when molecules of CaF₂ collide with already deposited material, the molecules do not move far and they form very fine microstructures. By contrast, SiO at about 70° polar angle produces a layered structure without well defined helices.

FIG. 6 is a micrograph of helical growths of MgF₂ on a glass substrate. Source material was evaporated by resistively heating a filled tantalum foil boat in a vacuum chamber with pressure 1×10^{-6} torr. The polar angle was 85° . The growth shown here used feedback from the deposition rate monitor to ensure a film growth with constant pitch (w). Helices of similar form have been grown with pitches ranging from 50 to 2,000 nm, and in films composed of MgF₂, SiO, CaF₂, Cr, Mn, Ag and Cu. It is believed on reasonable grounds that the process will work with any column forming depositable material. Depositable material is column forming when it exhibits limited adatom diffusion and a sufficiently high sticking factor that structures are formed, rather than unformed masses. Tests show that the MgF₂ helical film growths thus produced exhibit optical rotatory dispersion when $\lambda_{vac} > n_{avg} w$, where λ_{vac} is the wavelength of light in a vacuum and n_{avg} is the index of refraction of the MgF₂ film. The MgF₂ film has been found to exhibit optical rotation approximating 340 degrees/mm in a film with 17.3 turns and $w=360$ nm. Optical rotation for MgF₂ is counterclockwise for a right-handed helix, and clockwise for a left-handed helix.

As shown in FIG. 8, small mounds **80** may be micromachined or otherwise formed on the substrate **10** to form preferred locations for helical growths to initiate growth. The mounds **80** should be sufficiently close that shadowing effects prevent deposition of vapor between the mounds. In the case of mounds **80** having a height in the order of 1 micron, the mounds **80** should not be more than a few microns apart in case of the angle of incidence of the vapor being greater than 80° . The desired separation of the mounds **80** depends on the height of the mounds, the angle of incidence of the vapor, and the diffusion length of the vapor. An approximation of the separation L is given by $L = h \tan \theta$ where h is the height of the mounds. The mounds may have any shape, but the diameter is preferably selected so that only one column grows on each mound. The mounds **80** restrict growth of helices to the mounds **80**, and thus the growths can be forced to grow in specific locations. Various patterns of mounds for growing helical columns can be made such as one shown in FIG. 9. The mounds can be used

to grow slanted columns (no rotation of the substrate), and can be used to grow helices (with rotation of the substrate). Control of the separation of the columnar growths is believed to be useful in applications such as operation of the thin film microstructure as a delay line, where the acoustic wave characteristics depend on the spacing of the helical columns, or use of the thin film microstructure as a biological filter.

Applications for the sculpted thin film helical growths described here include uses as helicoidal bianisotropic media, which are useful in a wide range of applications, as for example as isolators, circular polarizers, quarter-wave and half-wave plates, frequency converters and notch filters. When used as helicoidal bianisotropic media, the vapor deposited material should be at least partially transparent at the wavelength of the electromagnetic radiation of interest. The helical growths **70**, illustrated in FIG. 7A, deposited on a substrate **10**, and grown with rotation of the substrate about a normal to the surface of the substrate, (with or without capping) may be sandwiched between two transparent charged electrodes **72** as shown in FIG. 7C. The electrodes **72** are shown schematically and in practice may be thicker. The electrodes **72** may be made from indium tin oxide or other transparent electrically conducting material and preferably take the form of plates. The cap **74** is preferably made from the same material as the helical growths, but need not be. When used with bounding electrodes such as those shown in FIG. 7C, the cap **74** and substrate **10** act as insulators. If insulators are not required in an application, then the substrate **10** may be conducting and the cap may form the upper electrode. The structure shown in FIG. 7C may be used as an optical filter for circularly polarized light. By applying a charge to the electrodes **72**, the electrodes **72** may be pulled together or pushed apart and thus change the pitch of the helices **70**. This has the effect of tuning the filter created by the thin film.

In a further application, particularly of the helical growths **70** as illustrated in FIG. 7B with a cap **74**, pairs of electrodes **76** and **78** may be placed at opposed ends of the structure spaced from each other. A varying voltage may be applied to one electrode **76** to sequentially compress and expand the structure, with the helical columns thus functioning as microscopic springs, in a direction parallel to the helices **70** in accordance with the varying voltage. The series of compressions and expansions will then propagate along the structure as an acoustic wave to the other end where the electrodes **78**, acting as a capacitive acoustic wave sensor, convert the acoustic wave to an electrical signal. Such a device may act for example as an electronic delay line, with a long delay in a very short structure.

Other applications for the thin films described here include use as electroluminescent devices wherein the substrate is formed of a metal, and the columnar growths are oxidized and crystallized to generate an array of quantum wires.

The quantum wire array may be ion-etched to remove the topmost oxide and overcoated with a transparent conductor under conditions that lead to a dense film. The lid would also provide electrical continuity to all wires. Polarizing, retarding, and/or optical interference coatings can be deposited over the transparent conductor in order to tailor the wavelength, the polarization, and the intensity of the emitted light.

Sculpted thin films can also be designed consisting of a highly porous thick retarder film on top of a transparent substrate. An optical sensing system may use a linearly

polarized laser beam to illuminate the film so as to yield a half-wave phase-shift at the appropriate laser wavelength. Adsorption of a chemical or biological species on the pore surfaces gives rise to small but detectable changes in the birefringence. This, in turn, generates a non-zero detector signal when viewed through a polarizer parallel to the incident laser beam.

A more advanced method uses a similar optical configuration but with coil elements (helical columns). In this case, the combination of birefringence and optical rotation will give a complex spatial irradiance pattern at the detector which can be detected with a two-dimensional array. The changes in this pattern may provide a recognizable optical signature of the adsorbed species. Through the use of pattern recognition techniques, a single sculpted thin film may thus be able to distinguish a wider range of chemical species than existing devices. Such chemical sensors will combine the high sensitivity of a large surface-to-volume ratio with optical phase detection. They operate on the principle that the interface dipoles associated with an effective fractional monolayer's coverage are sufficient to generate a detectable change in the birefringence and optical rotation of the films (which can be modeled with the use of known effective medium theories).

In addition, because the sculpted thin films are porous they can be impregnated with molecular monolayers or discrete clusters designed to react with specific chemical species. Alternatively, they can act as catalyst supports such that catalytic reactions take place and are sensed when a properly dispersed catalyst is exposed to gases.

Sculpted thin films as made in accordance with the invention may also be used as micro-sieves. Columnar sculpted thin films are highly porous, the backbone elements taking up about 10–30% of space. After a STF has been made, it may be dipped in a chemical bath to conformally coat the backbone elements with selected chemicals. When a biological fluid is forced through the micro-sieve thus made, particles in the fluid interact with the chemicals over large surface areas and are filtered out. This is believed to be particularly effective for particles of linear dimensions 10–50 nm. As described earlier, the backbone elements can be cleverly designed to fit the particle shapes, much as a key fits a lock.

In a different approach for realizing micro-sieves, the void regions of a columnar thin film may be filled with some material (e.g. a polymer) and the initial material then removed, leaving the replateform with 70–90% space filled and embedded sculpted thin film void nanostructure. The resulting nanostructure would be smaller in volume (10–30%) as well as in size (30–100 nm). With this extension to the manufacture of sculpted thin films, the matrix as well as the void phases can be varied continuously from 10% to 90% while still retaining large internal surface area.

Thus, a sculpted thin film micro-sieve may serve as a trap or filter for viruses quite effectively. Another use of a micro-sieve may be to provide a biocompatible substrate for tissue to grow on. Two bone fragments can possibly be joined by placing a sculpted thin film in between them and letting tissue grow through the thin film. Likewise, tissue can be made to grow on a biocompatible sculpted thin film attached to a prosthetic device. The replateform approach based upon natural structures, such as corals, is currently used commercially for biomedical applications.

Other uses for thin films with helical growths include applications in semiconductor integrated circuit fabrication such as very low dielectric insulators for high speed devices,

thermal barrier coatings on high temperature cycling parts such as jet turbine blades, flat panel displays, thermoelectric cooling panels, solar absorbers, adhesive surfaces, electron emitters, tactile sensing for smart skins, magnetic devices, anti-reflection/low dielectric constant coatings, humidity 5 sensing and microfluid pumping systems.

The technique of changing the polar angle after columnar deposition may be used to cap films with slanted, curved, vertical or other variably shaped columns.

A cap for a porous microstructure may also be formed by 10 exposing the porous microstructure to conditions in which the atoms in the vapor flux have a higher diffusion length than during formation of the porous microstructure, as by changing the substrate temperature or changing to a lower melting point material in the vapor flux. It will be understood that in performing the inventive steps described herein the film composition may be altered during deposition by 15 changing the material in the vapour flux. This may occur during formation of a porous microstructure, immediately before capping, or even during capping to form a layer, composite structure.

A person skilled in the art could make immaterial modifications to the invention described in this patent document without departing from the essence of the invention that is 25 intended to be covered by the scope of the claims that follow.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method of sculpting vapor deposited thin films, the method comprising the steps of:

initially exposing a surface of a substrate to a vapor flux 30 of material at an oblique incident angle to grow a columnar thin film formed of columns of the material; and

subsequently, and while continuing to expose the surface 35 to the vapor flux, rotating the substrate about an axis parallel to the plane of the substrate.

2. The method of claim 1 further comprising, while initially exposing the substrate to the vapor flux, moving the 40 substrate to alter the direction of growth of the columns.

3. The method of claim 2 in which moving the substrate to alter the direction of growth includes rotating the substrate about a normal to the surface of the substrate.

4. The method of claim 3 in which:

the substrate is rotated about a normal to the surface to 45 establish a helical thin film growth, during a first depositional period of time without rotation about the axis parallel to the plane of the substrate; and

the substrate is rotated during a second depositional 50 period of time about the axis parallel to the plane of the substrate to form a cap for the helical thin film growth.

5. The method of claim 4 in which the substrate is rotated about the normal axis during the second depositional period.

6. The method of claim 4 in which the angle of the 55 substrate to the vapor flux is maintained constant during the first depositional period at an angle greater than 80°.

7. A method of sculpting vapor deposited thin films, the method comprising the steps of

establishing, in a computer, a desired pattern of thin film growth;

while exposing a surface of a substrate to a vapor flux at an oblique incident angle, rotating the substrate about a normal to the surface;

providing control signals to the computer indicative of thin film growth on the substrate; and

automatically controlling the rotation speed of the substrate in response to the control signals to form distinct helical columns of material on the substrate.

8. The method of claim 7 further comprising forming a cap on the distinct helical columns by depositing material, after formation of the distinct helical columns, under conditions such that gaps between the distinct helical columns are filled in.

9. The method of claim 8 in which the gaps between the distinct helical columns are filled in by heating the surface of the substrate during deposition of the vapor flux.

10. The method of claim 7 further comprising:

rotating the substrate about an axis parallel to the plane of the substrate to form a cap on the distinct helical columns.

11. A method of sculpting vapor deposited thin films, the method comprising the steps of:

exposing a surface of a substrate to a vapor flux at an oblique incident angle; and, at the same time,

rotating the substrate about a normal to the surface while maintaining the oblique angle at greater than 80° to a normal to the surface of the substrate, so as to form distinct helical columns of material on the substrate.

12. The method of claim 11 further including forming a cap on the distinct helical columns.

13. The method of claim 12 in which forming a cap comprises rotating the substrate about an axis parallel to the surface of the substrate while exposing the substrate to the vapor flux.

14. The method of claim 12 in which forming a cap comprises exposing the substrate to vapor flux under conditions such that gaps between the distinct helical columns are filled in.

15. The method of claim 14 in which the gaps between the distinct helical columns are filled in by heating the substrate during deposition of the vapor flux.

16. A method of growing thin film microstructures on a substrate exposed to a vapor flux at an oblique angle of incidence, the method comprising the steps of:

forming mounds on the substrate, the mounds being separated by sufficient distance that vapor is not deposited between the mounds; and

exposing the surface of the substrate to a vapor flux at an oblique incident angle to grow a columnar thin film on the mounds, with one column on each mound.

17. The method of claim 16 further including:

rotating the substrate about a normal to the substrate during deposition to create helical growths.

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